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Inductively Coupled Plasma Mass Spectrometry for Trace Element Analysis by SW-846 Method 6020A/B

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1.0 Scope and Application

1.1 This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on EPA Method 6020A and 6020B.

1.2 Method 6020A and 6020B lists twenty-three elements approved for analysis by ICP-MS. The laboratory has implemented analysis by these methods for : Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mg, Mn, Ni, Se, Ag, Sr, Tl, Th, V, and Zn. Additional elements may be included provided that the method performance criteria presented in Sections 9 and 12 are met. Project approval may be required from the controlling agencies for compliance testing beyond the elements included in the promulgated methods and for those elements which may require state-specific accreditation.

1.3 The procedure is applicable to the analysis of acid digested waters, sediments, sludges and soils. Standard reporting limits are listed in Attachment 1 for water and soil. The preliminary acid digestion for aqueous samples is described in SOP DV-IP-0014 for Methods 3005A and 3020A and the digestion procedure for solids is given in SOP DV-IP-0015 for Method 3050B.

2.0 Summary of Method

2.1 Aqueous digestates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radiofrequency (RF) plasma. There the sample is decomposed and desolvated.

2.2 The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a mass resolution better than or equal to 0.9 amu (see Section 3) peak width at 10% of the peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier.

2.3 A collision/reaction cell utilizing He and (optionally) H_2 gases is used to remove molecular interferences. As the ion beam passes through the cell chamber, a diffuse cloud of He or H_2 gas is injected into its path. Collisions between the ions and the atoms in the gas deflect and remove interferences. See Section 4.2.3 for more information.

2.4 Interferences must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference corrections must include compensation for background ions contributed by the plasma gas, reagents, and the constituents of the sample matrix. Recommended elemental equations, which correct for many of these interferences, are listed in Attachment 2. Interference equations may vary or be unnecessary depending on the instrument setup and choice of collision/reaction gas.

2.5 Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices. Internal standard assignments are listed in Attachment 4.

3.0 Definitions

3.1 Atomic Mass Unit (amu) – Obsolete term replaced by “unified atomic mass unit (u)” or “dalton (Da)”, which denotes a small unit of mass that is used to express atomic and molecular masses. It is defined to be 1/12 of the mass of one atom of carbon-12.

3.2 Batch – The batch is a set of up to 20 samples of the same or similar matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches are defined at the sample preparation stage. See Policy DV-QA-003P for further details.

3.3 Dissolved Metals - Those elements which pass through a 0.45-μm membrane filter (sample is acidified after filtration).

3.4 Total Metals - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.5 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.6 Instrument Detection Limit (IDL) - See Section 12.3.

3.7 Sensitivity - The slope of the analytical curve (i.e., the functional relationship between raw instrument signal and the concentration).

3.8 Tuning Solution - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.9 Initial Calibration Verification / Quality Control Standard (ICV) - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.10 Continuing Calibration Verification (CCV) - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.11 Interference Check Standard (ICS) - A solution containing both interfering and analyte elements of known concentration that is used to correction factors.

3.12 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB) - A multi-element standard of known concentrations that is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.13 Reagent Blank - High purity (> 18 megohm-cm) water containing the same acid matrix as the calibration standards that is carried through the entire digestion process.

3.14 Calibration Blank - High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples. Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.15 Method Detection Limit (MDL) - The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

3.16 Low Level ICV (LLICV) / Continuing Calibration Verification (LLCCV) - A multi-element standard of known concentrations prepared to monitor and verify the instrument performance at the reporting limit (RL).

3.17 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 <u>Interferences</u>

4.1 Elemental Isobaric Interferences

Elemental isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software and by the careful selection of isotopes for analysis.

4.2 Isobaric Molecular Interferences

4.2.1 Polyatomic interferences are derived from the plasma gas, reagents or sample matrix. Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Attachment 3 lists isobaric interferences which might possibly affect required analytes. These molecular interferences are minimized by use of the collision cell utilizing He and/or H_2 gases. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.

4.2.2 Chloride in samples can produce low recoveries for antimony and silver. If chloride interference is a concern, 1% HCl can be added during digestion, but calibration standards must be adjusted to include 1% HCl also. The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

4.2.3 Collision cell interference removal works both by causing the interfering molecular ion to dissociate and by reducing the kinetic energy of the ion. The latter is termed Kinetic Energy Discrimination (KED), and is the primary mechanism for interference removal. Polyatomic ions are larger than elemental ions and so collide with the helium atoms in the collision

cell more frequently than the smaller elemental ions. Each collision reduces the energy of the ion, so the molecular ions lose energy more quickly. At the end of the collision cell a positive voltage plate prevents passage of the now low energy molecular ions. Thus, the interference is eliminated because the molecular ions do not reach the detector.

4.3 Doubly Charged Ion Interferences

Doubly charged elemental ion interferences are possible in cases where the second ionization potential of the element is significantly below the first ionization potential for argon (15.7 eV). If a doubly charged ion is formed, it will cause a response at half of its elemental mass, potentially causing interference. Most elements have high enough second ionization potentials that formation of doubly charged ions is not an issue. The percentage of doubly charged ions being formed in the plasma is monitored on a daily basis during the instrument tuning process.

4.4 Physical Interferences

4.4.1 Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.4.2 Internal standards should be added at a level to give approximately 100,000 – 20,000,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte.

4.4.3 Matrix effects are monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020A, the internal standard recoveries in samples can not fall below 70% of the intensity of the calibration standard. For method 6020B, the internal standard recoveries in samples cannot fall below 30% while the requirement for DoD is 30-120%. If they fall outside the applicable window, a five-fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample is reanalyzed.

4.4.4 Memory effects or carry-over can occur when there are large relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use.

It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The ICP-MS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) capable of providing resolution less than or equal to 0.9 amu at 10% peak height and 1.0 amu at 5% peak height in the mass range from 6-253 with a data system that allows corrections for isobaric interferences and the application of the internal standard technique. The ICP-MS must be equipped with a collision cell for the removal of molecular interferences.

6.1.2 A four-channel peristaltic pump.

6.1.3 Autosampler with autosampler tubes.

6.1.4 Appropriate water cooling device.

6.2 Supplies

6.2.1 Argon gas: High purity grade (99.99%).

6.2.2 Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.2.3 Class A volumetric flasks.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All standards must be entered into the TestAmerica LIMS (TALS) Reagent Module. Reagents that are not used for calculating results may either be recorded in the Reagent Module or may be entered into batch worksheets.

7.1 Storage and Shelf-Life

7.1.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Standards stored at concentrations as received from the vendor and mid-level dilutions must be replaced prior to the expiration date assigned by the vendor. If no expiration date is provided, the stocks and mid-level standards may be stored for up to one

year. They must be replaced sooner if verification from an independent source indicates a problem.

7.1.2 Working standards, i.e., all standards at concentrations ready to analyze on the ICP-MS (except tuning mixes, ICSA and ICSAB mixes, which are received at ready-to-use concentrations) are prepared fresh daily.

7.1.3 For more information on standard storage and shelf-life, see SOP DV-QA-0015.

7.2 Standards

Detailed instructions regarding the preparation of standards and reagents are given in this section. Alternate procedures are allowed as necessary to accommodate volume requirements as long as final concentrations are maintained and an accurate description of the standard or reagent used is entered into the Reagent Module in TALS.

7.2.1 Tuning Solution

The parent tuning solution is purchased as a custom multi-element mix. The elements and concentrations of the constituents are shown in Attachment 7. Prepare the working tuning Solution as detailed below.

7.2.1.1 Obtain a clean 1 L volumetric flask

7.2.1.2 Place 500 mL of reagent water and 10 mL of conc. HNO3 in the flask

7.2.1.3 Pipette 1mL of the Tuning Solution Stock into the flask

7.2.1.4 For the Agilent 7700 also add 50 µL of a 500 mg/L Mg solution and 30 µL of a 1000 mg/L Be solution.

7.2.1.5 Dilute to volume with reagent blank (See Section 7.3). Stopper and mix.

7.2.2 P/A factor solution

7.2.2.1 The Pulse/Analog (P/A) solution is used to monitor the correlation between the Pulse counting and Analog modes of the electron multiplier. The diluted solution must be prepared at different concentrations depending on the current instrument conditions. Multiple dilutions may be required to cover the required intensity range for all elements.

7.2.2.2 The P/A solution may be commercially purchased as a custom multi-element mix. See Attachment 7 for a list of the constituents and concentrations.

7.2.2.3 Prepare and use the P/A solution as recommended by the instrument manufacturer. The P/A solution should be analyzed daily.

7.2.3 Calibration Standard

Stock calibration standards are purchased as custom multi-element mixes or as single element solutions. Each day of analysis, the standards are diluted to working levels using reagent blank (see Section 7.3). The concentrations are given in Attachment 10. Prepare the Daily Working Calibration Standard as shown.

7.2.3.1 Daily Working Calibration Standard for Instruments 077 and 078 (ms 77 cal std)

7.2.3.1.1 Obtain a clean 100 mL volumetric flask.

7.2.3.1.2 Place 50 mL of reagent blank in the flask.

7.2.3.1.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.3.1.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.3.1.5 Pipette 0.5 mL of the MS CALSTD-3 stock standard into the flask.

7.2.3.1.6 Pipette 0.5 mL of the MS BRC CALSTD stock standard into the flask.

7.2.3.1.7 Pipette 0.5 mL of a 20 mg/L Zr standard into the flask.

7.2.3.1.8 Pipette 0.5 mL of a 20mg/L Sr standard into the flask.

7.2.3.1.9 Pipette 0.5 mL of a 200 mg/L Li standard into the flask.

7.2.3.1.10 Dilute to volume with reagent blank. Stopper and mix.

7.2.4 Initial Calibration Verification (ICV) Standard

The ICV stock is from a source different than the source for the calibration standards. Each day of analysis, the ICV standards are prepared new in reagent blank to the concentrations shown in Attachment 10. Prepare the ICV as shown below:

7.2.4.1 Initial Calibration Verification Standard for Instruments 077 and 078 (MS 77 ICV)

7.2.4.1.1 Obtain a clean 50 mL volumetric flask.

7.2.4.1.2 Place 25 mL of reagent blank in the flask.

7.2.4.1.3 Pipette 0.1 mL of the MS ICV StockA Standard into the flask.

7.2.4.1.4 Pipette 0.1 mL of the MS ICV StockB Standard into the flask.

7.2.4.1.5 Pipette 0.1 mL of the MS ICV Alt HP Standard into the flask.

7.2.4.1.6 Pipette 0.1 mL of the MS ICV BRC HP Standard into the flask.

7.2.4.1.7 Pipette 0.1 mL of a 20 ug/L Sr standard into the flask.

7.2.4.1.8 Pipette 0.1 mL of a 200 ug/L Li standard into the flask.

7.2.4.1.9 Dilute to volume with reagent blank. Stopper and mix.

7.2.5 Continuing Calibration Verification (CCV) Standard

The CCV is prepared from the same source as the calibration standards. The CCV standards are prepared fresh each day of analysis in reagent blank. The concentration is shown in Attachment 10.

7.2.5.1 Continuing Calibration Verification for Instruments 077 and 078 (ms 77 ccv)

7.2.5.1.1 Obtain a clean 100 mL volumetric flask.

7.2.5.1.2 Place 50 mL of the Daily Working Calibration Standard in the flask.

7.2.5.1.3 Dilute to volume with reagent blank. Stopper and mix.

7.2.5.2 Continuing Calibration Verification for Instrument 024 (MS CCV)

7.2.5.2.1 Obtain a clean 100 mL volumetric flask.

7.2.5.2.2 Place 50 mL of reagent blank in the flask.

7.2.5.2.3 Pipette 0.25 mL of the MS CALSTD-1 stock standard into the flask.

7.2.5.2.4 Pipette 0.25 mL of the MS CALSTD-2 stock standard into the flask.

7.2.5.2.5 Pipette 0.25 mL of the MS CALSTD-3 stock standard into the flask.

7.2.5.2.6 Pipette 0.25 mL of a 20 mg/L W standard into the flask.

7.2.5.2.7 Dilute to volume with reagent blank. Stopper and mix.

7.2.6 Reporting Limit (RL) Standards

The reporting limit standards are prepared fresh daily from the same stock as the calibration standards using the reagent blank. The analyte concentrations must be less than or equal to the respective reporting limits. Multiple solutions may be required in order to satisfy all of the project and client specific reporting limits. Alternate reporting limit concentrations may be used as necessary to meet client requirements as long as an accurate description of the standard used is entered into the Reagents module in TALS. Prepare the Reporting Limit Standard for the Agilent 7700 as detailed below.

7.2.6.1 RL Standard for Instruments 077 and 078 (ms 77 RL)

7.2.6.1.1 Obtain a clean 50 mL volumetric flask.

7.2.6.1.2 Place 30 mL of reagent blank in the flask.

7.2.6.1.3 Pipette 0.5 mL of the ms 77 cal std solution into the flask.

7.2.6.1.4 Dilute to volume with reagent blank. Stopper and mix.

7.2.7 Daily Linear Range Standard

The Linear Range standard is prepared from the same stock as the calibration standards using reagent blank.

7.2.7.1 Daily Linear Range Standard for Instruments 077 and 078 (MS 77 LR STD)

7.2.7.1.1 Obtain a clean 500 mL volumetric flask.

7.2.7.1.2 Place 50 mL of reagent blank in the flask.

7.2.7.1.3 Pipette 1.0 mL of a 1,000 mg/L As standard into the flask.

7.2.7.1.4 Pipette 2.5 mL of a 1,000 mg/L Ba standard into the flask.

7.2.7.1.5 Pipette 1.0 mL of a 1,000 mg/L Be standard into the flask.

7.2.7.1.6 Pipette 1.0 mL of a 1,000 mg/L Cd standard into the flask.

7.2.7.1.7 Pipette 1.0 mL of a 1,000 mg/L Co standard into the flask.

7.2.7.1.8 Pipette 2.5 mL of a 1,000 mg/L Cr standard into the flask.

7.2.7.1.9 Pipette 2.5 mL of a 1,000 mg/L Cu standard into the flask.

7.2.7.1.10 Pipette 1.0 mL of a 1,000 mg/l Li standard into the flask.

7.2.7.1.11 Pipette 5.0 mL of a 1,000 mg/L Mn standard into the flask.

7.2.7.1.12 Pipette 1.0 mL of a 1,000 mg/L Mo standard into the flask.

7.2.7.1.13 Pipette 2.5 mL of a 1,000 mg/L Ni standard into the flask.

7.2.7.1.14 Pipette 2.5 mL of a 1,000 mg/L Pb standard into the flask.

7.2.7.1.15 Pipette 0.5 mL of a 1,000 mg/L Sb standard into the flask.

7.2.7.1.16 Pipette 1.0 mL of a 1,000 mg/L Se standard into the flask.

7.2.7.1.17 Pipette 1.0 mL of a 1,000 mg/L Sn standard into the flask.

7.2.7.1.18 Pipette 1.0 mL of a 1,000mg/l Sr standard into the flask.

7.2.7.1.19 Pipette 0.5 mL of a 1,000 mg/L Tl standard into the flask.

7.2.7.1.20 Pipette 1.0 mL of a 1,000 mg/L U standard into the flask.

7.2.7.1.21 Pipette 1.0 mL of a 1,000 mg/L V standard into the flask.

7.2.7.1.22 Pipette 2.5 mL of a 1,000 mg/L Zn standard into the flask.

7.2.7.1.23 Pipette 0.05 mL of a 10,000 mg/L Th standard into the flask.

7.2.7.1.24 Dilute to volume with reagent blank. Stopper and mix.

7.2.8 Internal Standard (IS) Solution (77 I.S. / MS I.S. INT)

The internal standard solution is added continuously by peristaltic pump through a mixing tee. The concentrations and components are specified in Attachment 4. Prepare the IS solution as follows:

7.2.8.1 Obtain a clean 250 mL volumetric flask.

7.2.8.2 Place 100 mL of reagent blank in the flask.

7.2.8.3 Pipette 1.2 mL of the 1,000 mg/L Ge Standard into the flask.

7.2.8.4 Pipette 0.4 mL of the 1,000 mg/L Ho Standard into the flask.

7.2.8.5 Pipette 0.4 mL of the 1,000 mg/L In Standard into the flask.

7.2.8.6 Pipette 0.75 mL of the 1,000 mg/L Sc Standard into the flask.

7.2.8.7 Pipette 1.5 mL of the 1,000 mg/L ^{6}Li Standard into the flask.

7.2.8.8 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.9 Interference Check Standard Solutions (ICSA / ICSAB)

The interference check standard solution (ICSA) and the spiked interference check standard solution (ICSAB) are prepared as follows:

7.2.9.1 ICSA Standard (ms 77 icsa / MS ICSA)

7.2.9.1.1 Obtain a clean 100 mL volumetric flask.

7.2.9.1.2 Place 50 mL of reagent blank in the flask.

7.2.9.1.3 Pipette 10.0 mL of the MS ICSA STOCK standard into the flask.

7.2.9.1.4 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.9.2 ICSAB Standard (MS 77 ICSAB / MS ICSAB)

7.2.9.2.1 Obtain a clean 100 mL volumetric flask.

7.2.9.2.2 Place 50 mL of reagent blank in the flask.

7.2.9.2.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.9.2.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.9.2.5 Pipette 0.5 mL of the MS CALSTD-3 stock standard into the flask.

7.2.9.2.6 For the Agilent 7700 instruments pipette 0.5 mL of the MS BRC CALSTD stock standard into the flask.

7.2.9.2.7 For the Agilent 7700 instruments pipette 0.5 mL of a 20 mg/L Sr standard into the flask.

7.2.9.2.8 For the Agilent 7700 instruments pipette 0.5 mL of a 200 mg/L Li standard into the flask.

7.2.9.2.9 For the Agilent 7500 instrument pipette 0.5 mL of a 20 mg/L W standard into the flask.

7.2.9.2.10 Pipette 10.0 mL of the MS ICSA STOCK standard into the flask.

7.2.9.2.11 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.10 6020A only -Low Level Initial Calibration Verification and Low-Level Continuing Verifications (ms 77 LLCCV / MS LCCV)

The low level ICV / low level CCV solution is prepared from the same source as the calibration standards. The low level standard is prepared fresh each day of analysis in reagent blank. The concentration is shown in Attachment 10. Prepare the low level standard solution as follows:

7.2.10.1 Obtain 2 clean 100 mL volumetric flask.

7.2.10.2 Place 50 mL of reagent blank in each flask.

7.2.10.3 Prepare a working standard by adding 0.5 ml of a 1000mg/l Li and 0.1ml of a 20mg/l Sr to the first flask and bring to volume.

7.2.10.4 Pipette 1.0 mL of the MS LLCCV1 stock standard into the second flask.

7.2.10.5 Pipette 1.0 mL of the MS LLCCV 2A stock standard into the second flask.

7.2.10.6 Pipette 1.0 ml of working standard for Sr and Li into the second flask.

7.2.10.7 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.3 Reagents

7.3.1 **Reagent Water –** Water free of the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.3.2 **Reagent Blank - Agilent 7700, 2% HNO3/0.5% HCl –** Carefully dilute 40 mL of concentrated HNO3 and 10 mL of HCl in 2.0 L of reagent water. This solution is used to dilute samples and it is used for the initial and continuing calibration blanks.

7.3.3 **Reagent Blank - Agilent 7700, 5% HNO3/5% HCL (Zr only) –** Carefully dilute 100 ml of concentrated HNO_3 and 100 ml if HCL in 2.0 L of reagent water. This solution is used to dilute samples and it is used for calibration blanks.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time[1]	Reference
Water[2]	HDPE	50 mLs	HNO_3, pH < 2	180 Days	SW-846
Soil	Glass	4 oz	Cool $\leq 6^{\circ}C$[3]	180 Days	SW-846

[1]Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Holding Times are calculated from the date the sample was collected.

[2]Water samples collected for dissolved elements are filtered immediately on-site by the sampler before adding preservative.

[3]Although ICP analysis of soil does not require refrigeration of the samples, mercury analysis does require refrigeration per SW-846. Samples which will be used to aliquot for both analyses must be refrigerated. Therefore the laboratory routinely refrigerates samples to be analyzed by Methods 6020A or 6020B.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply. Quality control requirements are summarized in Attachment 9.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Method Blank (MB)

For aqueous and soil samples, the method blank consists of reagent water that has been processed in the same manner as the samples. For soil samples analyzed under DoD QAPPs, the method blank consists of <1 mm glass beads that have been processed in the same manner as the samples. One method blank must be processed with each preparation batch.

Acceptance Criteria: Method blank results are acceptable if the concentration for each analyte of interest is less than ½ the reporting limit (RL). For DoD QSM 5.0 the control limit is less than ½ LOQ. In the absence of project specific reporting limits, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable.

Corrective Action: If the method blank does not meet the acceptance criteria, the source of contamination should be investigated to determine if the problem can be minimized or eliminated. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following

circumstances, may be reported as qualified (qualifier flags or narrative comments):

- The same analyte was not detected in the associated samples;
- The method blank concentration is less than 1/10 of the measured concentration of any sample in the batch;
- The method blank concentration is less than 1/10 the specified regulatory limit; or
- The analyte is a common laboratory contaminant (e.g., copper, zinc, iron, or lead) less than 2 times the RL. Note that some programs do not recognize common lab contaminants or have a more stringent criterion (e.g., DoD QSM 5.0 allows common laboratory contaminants up to the RL).

If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.3 Laboratory Control Sample (LCS)

The LCS consists of reagent water that is spiked with the analytes of interest at the project specific action level or, when lacking specific action levels, at approximately the mid-point of the calibration range (summarized in Attachment 10). For soil samples analyzed under DoD QAPPs, the LCS consists of <1 mm glass beads that have been spiked with the analytes of interest and processed in the same manner as the samples. One LCS must be processed for each preparation batch.

Acceptance Criteria: LCS control limits are based on three standard deviations of past laboratory results or program specific requirements. These limits must not exceed 80-120%. The control limits are maintained in TALS. For DoD QSM 5.0 the laboratory must use QSM Appendix C Limits for batch control if project limits are not specified.

Corrective Action: If the LCS recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reanalyzed One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples. If project requirements allow this exception, the data may be accepted with qualifiers, an NCM must be generated, and the failure narrated in the final report.

9.4 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

The MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest at the same level as the LCS (summarized in Attachment 10). An MSD is prepared by taking a third aliquot of the selected sample and spiking it with the analytes of interest at the same level as the LCS (summarized in Attachment 10). The MS and MSD are processed in the same manner as the samples. One MS/MSD pair must be processed for each preparation batch. Some programs (e.g., DoD) require that matrix spikes can be performed only on project samples, and that the samples to be used are identified on the chain of custody form. The spike concentration should be the same level as the LCS.

Acceptance Criteria: Control limits are based on historical data or project specific requirements. Historical control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 75-125% recovery, and 20% relative percent difference (RPD). The control limits are maintained in TALS. For DoD QSM 5.0 the laboratory must use QSM Appendix C limits for batch control if project limits are not specified.

Corrective Actions: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly (e.g., very low or very high recoveries);
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering peaks seen on chromatograms, or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.
- If both the parent sample and associated matrix spike results are over range the parent and the spikes shall be diluted by the same amount and the results from the reanalysis reported for both. If the

analyte concentration in the parent sample is greater than four times the concentration of spike added, then spike recovery results are not compared to control limits, and the recovery is either reported as "NC" (not calculated) or with a qualifier flag to indicate that the spike was less than four times the analyte concentration in the sample. If the dilution will cause the spike to be less than two times the reporting limit, the MS/MSD do not need to be diluted and the recovery reported as "NC" (not calculated).

- For MS/MSD that serve as batch QC, if the parent sample result is within the calibration range and the MS/MSD results are above the calibration range, the results are reported with the MS/MSD result being flagged as an over-range measurement (e.g., the E-flag qualifier).
- If the MS/MSD are client requested, the parent sample result is within calibration range and the MS/MSD results are above the calibration range, the sample and spike should be diluted, keeping in mind that we need to assess whether or not the dilution will best serve the client's needs. Consult with the PM as needed. Both the parent sample and MS/MSD samples must have the same dilution factor. Some EDDs do not accept data that are at different dilution factors.
- If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated) and the appropriate qualifier flags are added.

NOTE: See Denver Policy Memorandum P16-001 and Corporate Policy Memorandum CA-Q-QM-013 for more detail.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD is preferred as not all samples will contain measurable concentrations of the target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, an LCS and LCSD will be used to measure precision.

9.5 Interference Check Solutions (ICSA/ICSAB)

The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Attachment 5. The interference check solutions must be analyzed at the beginning of every analytical run and once every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences.

Acceptance Criteria: The non-spiked analytes in the A solution must be less than 2x the RL. The results for the trace elements (B portion) must be ± 20% of the expected value. In addition, the internal standard recoveries for both the ICSA and AB must be within 70-150% for Method 6020A, 30-150% for Method 6020B and 30-120% for DoD. Some programs have control limits for the non-spiked elements in the ICSA. Please check the client specific requirements. For DoD QSM 5.0 the ICSA for non-spiked elements is controlled to less than the absolute value of the LOD unless they are a verified impurity.

Corrective Action: If the ICSAB results exceed the 20% limit or the ICSA is out for DoD QSM 5.0, then the analysis sequence must be terminated. For DoD QSM 5.0 if the ICSA is outside of the control limits for the non-spiked elements the sequence must also be terminated. The problem must be investigated and fixed. The ICSA and all affected samples must be re-analyzed.

NOTE: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (e.g., ICPAES), acceptance criteria will be applied at that level and the data accepted.

9.6 Internal Standards Evaluation for Samples

The IS recovery in samples cannot fall below 70% or be above 150% of the intensity of the calibration blank for 6020A and 30-150% for 6020B. If sample IS recoveries fall outside of these criteria, a five-fold (1:4) dilution must be performed, the dilution analyzed, and the same acceptance criteria applied. For DoD QSM 5.0 the internal standard for samples is controlled to 30-120%.

9.7 Serial Dilution

One serial five-fold dilution should be analyzed per preparation batch. If the analyte concentration is within the linear range of the instrument and sufficiently high (minimally, a factor of 50 times above the MDL), the serial dilution must agree to within 10% of the original analysis. If not, an interference effect is suspected, which must be described in an NCM and included in the final report narrative. Samples identified as blanks should not be used for serial dilution. For DoD QSM 5.0 the serial dilution is evaluated if the parent sample concentration is greater than 50x the

LOQ prior to dilution. If the acceptance criteria are not met then the parent sample is flagged “J”. Method 6020B sets the calculation level at 25x RL and the required limit at 20%.

9.8 Post-Digestion Spike Addition (PDS)

A PDS is performed for each batch. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80 - 120% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected. Typically the concentration of the PDS is 200 µg/L for each element except silver which is spiked at 50 µg/L. For DoD QSM 5.0 if the parent sample concentration is less than 50x the LOQ prior to dilution then the PDS must recover within 80-120%. If the recovery is outside of the control limits for a given element then the parent sample is flagged “J”. Method 6020B allows limits of ± 25%.

9.9 Linear Range Verification (LRA/LRC)

The LDRs should be verified whenever, in the judgment of the analyst, a change in the analytical performance caused by either a change in instrument hardware or operating conditions would dictate the necessity to re-establish them. 6020B and DoD QSM require verification of linear ranges in each analytical run. As described in Section 7.2.7, a lower concentration is used for the daily check than is used for the quarterly determination.

Acceptance Criteria: The result for this standard must be within 10% of the expected value.

Corrective Action: If the Linear Range Verification standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analyst must run a standard at a lower concentration until the criteria is met or the samples cannot exceed the level of the highest calibration standard.

10.0 <u>Procedure</u>

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure identified after the work has been completed must also be documented in an NCM, with a cause and corrective action described.

10.3 Instrument Maintenance

See Section 20 in the QAM

10.4 Instrument Troubleshooting

See Attachment 11

10.5 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0014 and DV-IP-0015).

10.6 Calibration

10.6.1 Instrument Start Up

Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning. It is recommended that the instrument be flushed with the ICSA solution to help condition the cones and improve stability. Allow the instrument time to rinse completely before tuning the instrument.

10.6.2 Oxide\Doubly Charge Performance Check

With the sample probe in the Tune solution verify that the oxides and doubly charged ions are less the 3% by running the Tune report.

10.6.3 Instrument Tuning / Mass Calibration

Tune the instrument with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 5 times. Mass calibration and resolution checks using the tuning solution must be completed at the beginning of every day. If either of the following conditions fails the instrument setup must be re-evaluated and the solution rerun.

Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

Mass Resolution Check - The resolution at 5% peak height should be approximately 0.75amu.

NOTE: Method 6020B states to use the manufacturer's instructions for the tune. Since the laboratory may perform analysis for Method 6020A on the same instrument, the same requirements are applied to both.

10.6.4 Initial Calibration

The ICP-MS is calibrated each day of operation using a blank and a single standard (see Section 7.2.3). At least three integrations are employed. The validity of the calibration is determined by the subsequent calibration verifications, which are performed at concentrations as described in the next sections.

10.6.5 Low-Level Initial Calibration Verification (LLICV/ICVL)

A low-level ICV standard at or below the reporting limit (see Section 7.2.10) is analyzed after the initial calibration for Method 6020A. This is a standard obtained from the same vendor used for calibration.

Acceptance Criteria: The ICVL recovery must be within 70-130%.

The ICVL can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICVL results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.6.6 Mid-Level Second-Source Initial Calibration Verification (ICV)

A 40 µg/L ICV standard (see Section 7.2.4) is analyzed immediately after the initial calibration. This is a standard obtained from a different vendor than the standard used for calibration.

Acceptance Criteria: The ICV recovery must be within 90-110%. The ICV can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.6.7 Calibration Blank

An initial calibration blank (ICB) is analyzed after the ICV. Continuing calibration blanks (CCBs) are analyzed after each continuing calibration verification. The appropriate reagent blank is used for the blanks.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as zinc and iron must be less than the RL. In addition, the internal standard recoveries must be within 70-150% of the associated calibration blank for Method 8020A or

30-150% for Method 6020B. Client specific requirements take precedence. DoD QSM 5.0 requires control of blanks to a concentration less than or equal to the LOD with the internal standard recoveries of 30-120%.

Corrective Action: If the calibration blank exceeds acceptance limits, then the possibility of instrument contamination should be examined, particularly the possibility of carry-over from high level samples. The blank can be reanalyzed, and if successful, analysis can continue. However, samples tested after high-level samples should be retested. If the reanalysis is not successful, then the analysis should be terminated. After the problem is corrected, recalibrate and reanalyze all samples tested since the last acceptable CCB.

10.6.8 Reporting Limit (RL/CRI) Verification Standard

Because the ICP-MS calibration does not include multiple calibration levels, an independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. The RL verification standard (see Section 7.2.6) is analyzed after the daily ICB.

Acceptance Criteria: For Method 6020A, the results should be within 50% of the expected value. Some programs may require tighter controls. For Method 6020B and DoD QSM 5.0 the control limits are 80-120%.

Corrective Action: If the RL verification fails to meet acceptance limits, data for the associated samples must be assessed. For example, if the results are high, consider blank contamination, and if the results are low, consider MDL verifications. At a minimum, sample results must be qualified in the final report. For DoD QSM 5.0, if the low-level standard does not meet the limits when spiked at the required project RL, the run sequence must be terminated.

10.6.9 Lower Limit of Quantitation Check (LLQC, LLOQ)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits, quarterly and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the RL is that this standard is carried through the entire preparation and analytical procedure. Prepare 7 aliqouts.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 35% of their true value. The RSD should be ≤20%

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.6.10 6020A Only - Low-Continuing Calibration Verification (LLCCV/CCVL) Standard

A low-level CCV standard is analyzed after every set of ten samples and at the end of the analytical sequence.

Acceptance Criteria: The CCVL recovery must be within 70-130%. In addition, the IS recovery must be within method limits. If CCVL results are not within these limits, the CCVL can be reanalyzed, but it must be successful twice in succession. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the CCVL standard successfully analyzed.

For the state of Washington the CCVL must work on the first attempt.

Corrective Action: If the CCVL fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCVL. If the associated samples are at levels greater than 10X the level of the CCVL the data may be considered acceptable but the failure must be documented with an NCM and addressed in the case narrative.

For the state of Washington the previous 10 samples must be reanalyzed. A recalibration is not necessary if the two CCVL's following the failure are successful but the samples must still be rerun.

10.6.11 Continuing Calibration Verification (CCV) Standard

A 50 μg/L CCV standard (see Section 7.2.5) is analyzed after every set of ten samples or every 2 hours, whichever is most frequent, and at the end of the analytical sequence.

Acceptance Criteria: The CCV recovery must be within 90-110%. In addition, the IS recovery must be within 70-150% for Method 6020A or 30-150% for Method 6020B. If the CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession or further corrective action must be taken.

For the state of Washington the CCV must work on the first attempt

Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCV.

For the state of Washington the previous 10 samples must be reanalyzed. A recalibration is not necessary if the two CCV's following the failure are successful but the samples must still be rerun.

10.7 Sample Analysis

10.7.1 Report the average of at least three integrations for all field and QC samples analyzed.

10.7.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

10.7.3 Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element. See Attachment 3 for examples.

10.7.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte. DoD QSM 5.0 requires that samples be diluted and reanalyzed if they are above the daily linear range check standard. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the RL. (The sample should be diluted to the approximate midrange of the analytical curve.) See Section 9.9 for the linear range verification requirements.

10.7.5 The analytical run sequence should be performed as follows to meet all quality control criteria:

Instrument initialization / Warm-Up
Tune instrument
Perform mass calibration
Perform resolution check
Validate tuning criteria
Calibration blank
Calibration standard

ICV
ICB
LLICV
RL verification standard
LLQC(as needed)
ICSA
ICSAB
LRA
CCV
CCB
LLCCV (6020B)
10 Samples (which can include all sample types)
CCV
CCB
LLCCV (6020B)
Reslope
CCV
CCB
LLCCV

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points*, and under the public folder, *Arizona Calibration Training*.

11.2 ICV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}}\right) \times 100\%$$

11.3 CCV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}}\right) \times 100\%$$

11.4 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{SSR - SR}}{\text{SA}}\right) \times 100\%$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

NOTE: When the sample concentration is less than the detection limit, use SR = 0 for the purpose of calculating %R.

11.5 The relative percent difference (RPD) between sample duplicates is calculated according to the following equation:

$$RPD = \left[\frac{DU1 - DU2}{\frac{1}{2}(DU1 + DU2)} \right] \times 100$$

Where:

$DU1$ = Sample result

$DU2$ = Sample duplicate result

11.6 The final concentration for an aqueous sample is calculated as follows:

$$\text{Result}\,(\mu g/L) = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

11.7 The concentration determined in digested solid samples when reported on a dry weight basis is as follows:

$$\text{Result}\,(\mu g/kg) = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested
S = Percent solids/100

11.8 Sample data are reviewed by the analyst (Level 1 data review) and documented on the data review checklist (See SOP DV-QA-0020). The data package is then submitted for level 2 review by another analyst or data reviewer. Second level review is documented on the same checklist initiated by the analyst. The data review process is explained in SOP DV-QA-0020.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is

present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD, DOE and TX TRPP projects, an MDL verification is performed quarterly.

12.2 MDL Verification (MDLV)

Calculated MDLs from the annual studies are subject to quarterly verification by analyzing an MDLV standard.

12.2.1 Prepare an MDLV standard at 2-4 times the calculated MDL concentration.

12.2.2 Analyze the MDLV standard immediately after each MDL study and quarterly thereafter. This standard is subject to the entire preparation and analysis process.

12.2.3 The calculated MDL is verified if the MDLV standard is detected, nominally signal to noise ratio > 3, under routine instrument conditions.

12.2.4 If the first MDLV is not detected, re-prepare the MDLV standard at twice the original concentration and analyze. The lowest concentration that produces a detectable signal will then be reported as the MDL.

12.3 Instrument Detection Limit Study

Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each analyte used for analysis in accordance with Policy DV-QA-014.

12.3.1 Pour out seven undigested calibration blanks and run them on three non-consecutive days.

12.3.2 Calculate the standard deviation for each day. The final IDL concentration is the average of the three daily standard deviation values.

12.3.3 Method 6020B requires an initial verification of the IDL using 10 replicates in a single analytical sequence but no longer requires quarterly verification. Reverification is required after major maintenance, such as changing the detector.

12.3.4 See Policy DV-QA-014P for a discussion of IDL studies and evaluation of IDL results.

12.4 Linear Dynamic Range (LDR)

12.4.1 The LDR must be determined initially (i.e., at initial setup) and then every three months for each analyte used on each instrument. The linear

range is the concentration above which results cannot be reported without dilution of the sample.

12.4.2 The LDR must be determined from a linear calibration prepared in the normal manner using the normal operating procedures described in Sections 10 and 11.

12.4.3 The LDR is determined by analyzing successively higher standard concentrations of the analytes of interest. A minimum of three standards are required for the initial and on-going studies, and one of the levels must be at the upper end of the range. The calculated concentrations must be within 10% of the stated concentrations.

12.4.4 The highest standard that meets this criterion defines the maximum concentration that can be reported for sample analysis without dilutions.

12.4.5 If the instrument is adjusted in any way that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

12.5 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.5.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.5.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.5.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.5.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.5.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.1 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A

new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Program*.

14.2 The following waste streams are produce when this method is carried out:

14.2.1 **Aqueous Acidic (Metals) -** Corrosive - Waste Stream J

14.2.2 **Expired reagents and standards –** Contact the Waste Coordinator.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.1.1 Method 6020A: *Inductively Coupled Plasma - Mass Spectrometry*, Revision 1, February 2007.

15.1.2 Method 6020B: Inductively Coupled Plasma - Mass Spectrometry, Revision 2, July 2014.

15.1.3 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.4 Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, Revision 1, July 1992.

15.1.5 Method 3050B, Acid Digestion of Sediments, sludges and soils, Rev. 2,

Dec. 1996.

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/20/2010

15.3 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 5, July 2013.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6020A	Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file with QA.
2	EPA 6020A	Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.
3	EPA 6020A	Corrective action for a PDS failure will be limited to flagging the PDS indicating the failed analyte and the recovery rather than diluting and reanalyzing the sample.
4	EPA 6020A	Internal standard recoveries are based on the intensities of the internal standards in the most recent calibration blank rather than the intensities of the internal standards in the initial calibration standard.
5	EPA 6020A	Method 6020A states that the dilution test is applicable if the matrix sample is at least 50x the reporting limit. TestAmerica uses the tighter limit of 50x the MDL.
6	EPA 6020B	Method 6020B states to tune the instrument according to manufacturer's instructions. TestAmerica continues to use the tune requirements in Method 6020A in order to be able to run samples by either method under the same tune.
7	EPA 6020B	Method 6020B does not include the analysis of the ICS-AB. TestAmerica continues to analyze this QC sample due to various program requirements.
8	EPA 6020A/B	The tuning criteria listed in method 200.8 for mass resolution is used to satisfy the requirements of method 6020A/B

17.0 Attachments

Attachment 1: Standard Reporting Limits for Water and Soil
Attachment 2: Recommended Elemental Equations
Attachment 3: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes
Attachment 4: Internal Standards and Corresponding Metals
Attachment 5: Interference Check Sample Components and Concentrations
Attachment 6: Suggested Mass Choices
Attachment 7: Tuning Solution and P/A Solution
Attachment 8: Suggested Tuning and Response Factor Criteria
Attachment 9: Summary of Quality Control Requirements
Attachment 10: Calibration, Calibration Verification, and Spike Concentrations
Attachment 11: Troubleshooting

18.0 Revision History

Revision 7, Dated 31 October 2017

- Annual Review
- Updated section 10.6.3 Mass Resolution criteria to method 200.8
- Added Section16 item 8 for Mass Resolution criteria

Revision 6, Dated 26 October 2016

- Updated sections 7.2.3.1.9, 7.2.4.1.8, 7.2.9.2.8 and 7.2.10 for how Sr and Li are prepared in the standards
- Updated Section 10.6.9 and Attachment 9 to reflect 6020B limits and use of in-house limits
- Updated Sections 10.6.10 and 10.6.11 for the state of Washington requirements
- Updated Section 15 for consistency with other SOPs to reflect reference for SW-846

Revision 5, Dated 28 September 2016

- Added Li and Sr as analytes to the SOP
- Revised Section 1.2 to more clearly identify elements addressed by this SOP
- Added prep method numbers to Sections 1.3 and 15
- Combined Footnotes 1 and 3 for table in Section 8.0 to eliminate redundancy
- Removed references to AFCEE throughout SOP; no longer utilize AFCEE protocols
- Expanded MS/MSD failure corrective action in Section 9.4 to reflect current policy
- Added note in Section 10.6.3 regarding Method 6020B requirements for tune
- Added LLICV acceptance criteria for Method 6020B, different from 6020A.
- Removed references to Instrument 24 (Agilent 7500) throughout
- Added requirements for IDLs by 6020B to Section 12.3
- Moved Section 12.5 to new Section 9.9
- Revised Sections 12.6 and 12.7 to reflect current practice
- Added Method exceptions 6 and 7 for Method 6020B where the laboratory performs a more stringent practice than required.

Revision 4, Dated 31 December 2015

- Added method 6020B
- Added 6020B limits to Section 9.7 and 9.8, SD and PDS
- Corrected references

Revision 3, Dated 30 April 2015

- Annual Review
- Language and formatting changes throughout
- Corrected tuning sample requirement from 4 replicates to five replicates
- Changed 12.4.2 to 12.5
- Added Section 2.1
- Added new Section 2.3 to describe reaction cell
- Added new Section 4.2.3
- Added batch definition
- Deleted Attachment 2
- Deleted Attachment 4
- Added new Attachment 1 standard reporting limits
- Section 4.3.2 enlarged expected IS intensities
- Integrated Sections 4.4 and 4.5 into 4.2
- Created new Section 4.3 Doubly charged ions
- Added new Section 6.2.3 volumetric flasks
- Section 7.2.1.4 corrected Mg addition to standard
- Section 7.2.2 replaced P/A section with same section from DV-MT-0025
- Added P/A section to Attachment 7
- Section 7.1.3 added reference to standards SOP
- Added all new standard prep information into Sections 7.2.3 – 7.2.9
- Section 9.3 changed spike level from midpoint of LR to midpoint of cal curve
- Added note to Section 9.4
- Changed timing of ICSA to beginning of analytical run and every 12 hours
- Changed concentration limits for SD in Section 9.7 to 50x MDL
- Added method modification 5 to address SD limit
- 10.6.7 added DoD 5.0 language to corrective action
- Removed Section 10.3
- 10.7.5 added DoD requirement to dilute above daily LR
- 11.5 Corrected RPD calculation
- 11.7 changed to dry weight correction
- 12.2.1 changed MDLV spike level to 2-4x MDL

Revision 2, dated 09 April 2014

- Annual review
- Updated Section 7.2 for standards to reference TALS for how to make
- Added Section 7.4.4 for 5%HNO3/5%HCL for Zirconium
- Added Section 10.4 for Maintenance
- Added Section 10.5 for Troubleshooting
- Updated Sections 9 and 10 to include requirements for DoD QSM 5.0
- Added reference to DoD QSM 5.0.

Revision 1, dated 15 July 2013

- Annual review
- Corrected formatting
- Added section 3.16
- Added reference to data review in section 10.7
- Added documentation information in section 11.8
- Added detail to note associated with section 14.2
- Updated reference in section 15.2
- Removed Attachment 13

Revision 0.3, dated 13 July 2012

- Revised standards preparation procedures in Section 7
- Added section 7.2.2
- Split acid diluent into two solutions depending upon instrument
- Updated standard mixes used to prepare standards; instrument specific mixes as needed
- Clarified requirements for preservation of soil samples for ICPMS only analysis, Section 8
- Revised list of common lab contaminants in method blank corrective action (Section 9.2)
- Added section 10.5.2: oxide/doubly charged performance check
- Updated Sections 9.2 and 10.5.7 to control method blanks and calibration blanks to ½ the RL
- Updated Sections 9.1, 10.1, 10.2 and 12.1 to reflect current practice.

Revision 0.2, dated 08 July 2011

- Added Section 4.4 on polyatomic interferences
- Added Instruments to Section 6.1
- Section 10.5.1 Added to condition cones with the ICSA solution
- Added Section 10.6.3 to reflect soil dilution practices
- Section 11.4 Corrected the RPD calculation
- Added section 11.1 referencing corporate SOP CA-Q-S-005 "Calibration Curves"
- Added section 12.2 "MDL Verification (MDLV)"
- Added Attachment 13 "ICP-MS Technical Data Review Checklist"

Attachment 1

Standard Reporting Limits for Water and Soil

Element Name	Element Symbol	Water (ug/L)	Soil (ug/Kg)
Aluminum	Al	50	5,000
Antimony	Sb	2.0	200
Arsenic	As	5.0	600
Barium	Ba	1.0	200
Beryllium	Be	1.0	100
Cadmium	Cd	1.0	100
Chromium	Cr	2.0	200
Cobalt	Co	1.0	100
Copper	Cu	2.0	250
Iron	Fe	50	5,000
Lead	Pb	1.0	150
Lithium	Li	50	5,000
Manganese	Mn	1.0	250
Molybdenum	Mo	2.0	200
Nickel	Ni	2.0	150
Selenium	Se	5.0	500
Silver	Ag	5.0	100
Strontium	Sr	10	100
Thallium	Tl	1.0	100
Thorium	Th	5.0	200
Tin	Sn	10	2,500
Tungsten	W	5.0	500
Uranium	U	1.0	100
Vanadium	V	5.0	500
Zinc	Zn	10	1,000
Zirconium	Zr	0.5	---

Attachment 2

Recommended Elemental Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

Where M = Total ion count rate at the specified mass.

Attachment 3

Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	**Hydroxyl**	**Nitrogen**	**Chlorine**	**Sulfur**	**Carbon**	**Other**
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

Attachment 3 (cont.)
Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Attachment 4
Internal Standards and Corresponding Metals

IS	ICP-MS 077/078
^{6}Li	Be
Sc	Li, Na, Mg, Al, K, Ca
Ge	Sr, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se
In	Mo, Ag, Cd, Sn, Sb, Ba
Ho	Tl, Pb, Th, U, W

Attachment 5
Interference Check Sample Components and Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	110.0
Ca	100.0	110.0
Fe	100.0	110.0
Mg	100.0	110.0
Na	100.0	110.0
P	100.0	100.0
K	100.0	110.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.1
Ti	2.0	2.0
As	0.0	0.1
Sb	0.0	0.1
Be	0.0	0.1
Ba	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Pb	0.0	0.1
Li	0.0	1.0
Mn	0.0	0.1
Ni	0.0	0.1
Nb	0.0	0.2
Pd	0.0	0.1
Pt	0.0	0.1
Se	0.0	0.1
Sr	0.0	0.1
Tl	0.0	0.1
Th	0.0	0.1
Sn	0.0	0.1
Ag	0.0	0.1
U	0.0	0.1
V	0.0	0.1
W	0.0	0.1
Zn	0.0	0.1

Attachment 6
Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"9"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
"7"	Lithium
24, **25**, **26**	Magnesium
"**55**"	Manganese
58, "**60**", 62, **61**, 64	Nickel
93	Niobium
105	Palladium
195	Platinum
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
"88"	Strontium
"**205**", 203	Thallium
232	Thorium
192	Tungsten
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
139	Lanthanum
118	Tin
238	Uranium
35, 37	Chlorine
98, 96, 92, **97**, 94, "95"	Molybdenum
72	Germanium (IS)
165	Holmium (IS)
115	Indium (IS)
6	Lithium (6+) (IS)
45	Scandium (IS)

Attachment 7: Tuning Solution and P/A Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below is a suggested solution covering a typical mass calibration range. Instrument manufacturer recommendations should be followed for tuning solutions.

The P/A solution is used to monitor the correlation between the Pulse and Analog parts of the electron multiplier. This solution is prepared at different concentrations depending on the current instrument conditions. The parent standard concentration is shown below.

Element	Tuning Concentration (µg/L)	P/A Concentration (mg/L)
Al		5
As		20
Ba	10	5
Be	10	20
Bi		5
Cd		20
Ce	10	
Co	10	5
Cr		5
Cu		5
Ge		10
In	10	5
Ir		5
^{6}Li		5
Li	10	
Lu		5
Mg	10	10
Mn		5
Mo		10
Na		5
Ni		10
Pb	10	10
Pd		10
Rh	10	
Ru		10
Sb		10
Sc		5
Sn		10
Sr		5
Tb		2.5
Th		50
Ti		50
Tl	10	50
U	10	50
V		50
Y	10	2.5
Zn		20

Attachment 8:

Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution:

Be	>1,000
Mg	>2,000
Rh	>20,000
Pb	>10,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Attachment 9:

Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
LLOQ (6020B only)	With initial setup, Quarterly and on an as needed basis	65 - 135% recovery or in-house limits	Terminate analysis; correct the problem; recalibrate.
LLICV (6020A only)	Beginning of every analytical run.	70 - 130% recovery. 6020A IS, 70-150% rec.	Terminate analysis; correct the problem; recalibrate.
ICV	Beginning of every analytical run.	90 - 110% recovery.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result is < ½ RL.	Terminate analysis; correct the problem; recalibrate.
LLCCV (6020A only)	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent.	70 - 130% recovery. 6020A IS, 70-150% rec.	See Section 10.6.10. Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.
CCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent.	90 - 110% recovery.	Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.

Attachment 9: Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
CCB	Immediately following each CCV.	The result must be < ½ RL. .	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCB.
ICSA	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.5
ICSAB	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.5
Method Blank	One per lot of 20 field samples or fewer.	The result must be < ½ RL. Sample results greater than 10x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Re-run once. If > ½ RL, redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Serial Dilution	One per batch of 20 field samples or fewer.	90 - 110% recovery	See Section 9.7 for additional requirements.
Post-Digestion Spike	One per batch of 20 field samples or fewer.	80-120% recovery	See Section 9.8.
Laboratory Control Sample	One per batch of 20 field samples or fewer.	Must be within laboratory control limits	See Section 9.3
Matrix Spike	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See Section 9.6 for additional requirements.

Attachment 10
Calibration, Calibration Verification, and Spike Concentrations

Element	Initial Calibration (µg/L)	ICV (µg/L)	CCV (µg/L)	LCS (µg/L)	MS/MSD (µg/L)	Post Digestion Spike (ug/L)
Aluminum	10000	40	50	400	400	20000
Antimony	100	40	50	40	40	200
Arsenic	100	40	50	40	40	200
Barium	100	40	50	40	40	200
Beryllium	100	40	50	40	40	200
Cadmium	100	40	50	40	40	200
Chromium	100	40	50	40	40	200
Cobalt	100	40	50	40	40	200
Copper	100	40	50	40	40	200
Iron	10000	4000	5000	400	400	20000
Lead	100	40	50	40	40	200
Lithium	1000	400	500	100	100	200
Manganese	100	40	50	40	40	200
Molybdenum	100	40	50	40	40	200
Nickel	100	40	50	40	40	200
Selenium	100	40	50	40	40	200
Silver	100	40	50	40	40	50
Strontium	100	40	50	40	40	200
Thallium	100	40	50	40	40	200
Thorium	100	40	50	40	40	--
Tin	100	40	50	40	40	200
Tungsten	100	40	50	40	40	200
Uranium	100	40	50	40	40	200
Vanadium	100	40	50	40	40	200
Zinc	100	40	50	40	40	200
Zirconium	100	40	50	40	40	--

This procedure has been developed for twenty elements. Additional elements may be included in the calibration solution at the above levels. Levels may be adjusted to meet specific regulatory or client programs.

Attachment 11

ICP-MS Troubleshooting Guide

Problem	Possible Cause/ Solution
High Calibration Blanks	Inspect historical blank data to determine root cause Inspect, clean or replace torch Inspect, clean or replace pump tubing or sample tubing Inspect, clean or replace nebulizer Remake blank solution Recalibrate instrument
Instrument Drift	Make sure instrument has warmed properly Condition cones to aid stability Reslope to correct for changing cone conditions during run Stop run, clean cones and start over with a new calibration
Erratic Readings, High RSDs	Check nebulizer pressure Check sample flow around the pump, adjust tension on pump tubing to ensure smooth flow Check for clogs in the uptake tubing, nebulizer, or valve Clean or replace nebulizer
Low Sensitivity	Clean cones Adjust lens voltages Remove and clean lens, remove and clean or replace reaction cell
Bad Tune: Bad Mass Cal	Adjust lens voltages, remove and clean lens
Bad Tune: High Oxides	Inspect, clean, or replace torch, nebulizer, and spray chamber

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